

Colloidal Microstructure and Polydispersity Effects

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Most naturally occurring colloids and many synthesised colloidal suspensions investigated in the past are significantly polydisperse with respect to particle sizes and pair interactions. For this reason and also for technical applications, it is very important to study the influence of polydispersity and of mixing of different particles on the microstructure, diffusion and rheology of colloidal dispersions.

Using various Ornstein-Zernike-type integral equation schemes (MSA, RMSA, HNCA, PY, and RY) we have made extensive studies on the effect of polydispersity and mixing on microstructural and dynamic properties (e.g. [1-4]).

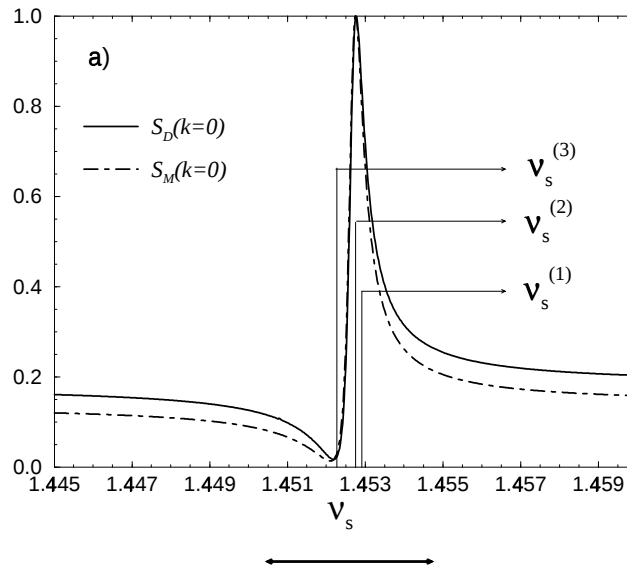


Figure 1: Small wave number limit of measured structure functions $S_M(0)$ and $S_D(0)$ vs ν_s for a 15 percent size-polydisperse charge-stabilised suspension of core-shell particles. The values $\nu_s^{(i)}$, for $i = 1, 2, 3$, correspond to three different definitions of solvent index matching (Refs. [3,4]).

As an example relevant for experimental applications, consider polydisperse suspensions of colloidal particles with an internal optical structure. This structure reflects the method of particle synthesis. The most prominent techniques to study the microstructure and dynamics of colloids involve the scattering of light. To avoid unwarranted multiple scattering of light, the refractive index contrast of the solvent with respect to the particles is minimized according to some prescribed criterion. To investigate the importance of contrast variation effects on the microstructure and short-time dynamics, we have calculated the measurable static structure factor $S_M(k)$ and the measurable hydrodynamic function $H_M(k)$ of size polydisperse colloidal particles with an internal optical structure [3,4]. The quantities $S_M(k)$ and $H_M(k)$ are the quantities determined in static and (short-time) dynamic light scattering experiments. Our detailed analysis shows that $S_M(k)$ and $H_M(k)$ are very sensitive to the refractive index contrast with respect to the solvent in the regime of strong index matching. This fact has important consequences for scattering experiments aimed to determine particles sizes and structural properties of colloidal dispersions.

Fig. 1 demonstrates the enormous variation of $S_M(k)$ at zero wavenumber as a function of the solvent refractive index ν_s , in the region of strong index matching indicated by the double arrow. The results shown in the figure describe size-polydisperse charge-stabilised colloidal particles with an internal core-shell structure. The function $S_D(k)$ is the result for $S_M(k)$ obtained from a simple approximative scheme (decoupling approximation) which can be easily implemented and which is in good agreement with $S_M(k)$ in the index matching regime.

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